



US009249324B2

(12) **United States Patent**
Li et al.

(10) **Patent No.:** **US 9,249,324 B2**
(45) **Date of Patent:** ***Feb. 2, 2016**

(54) **INK-JET INK COMPRISING CROSS-LINKED
PIGMENT DISPERSION BASED ON
POLYURETHANE DISPERSANTS**

(75) Inventors: **Xiaoqing Li**, Newark, DE (US); **Charles
T. Berge**, Earleville, MD (US)

(73) Assignee: **E I DU PONT DE NEMOURS AND
COMPANY**, Wilmington, DE (US)

(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 945 days.

This patent is subject to a terminal dis-
claimer.

(21) Appl. No.: **13/505,786**

(22) PCT Filed: **Nov. 19, 2010**

(86) PCT No.: **PCT/US2010/057356**

§ 371 (c)(1),
(2), (4) Date: **May 3, 2012**

(87) PCT Pub. No.: **WO2011/063190**

PCT Pub. Date: **May 26, 2011**

(65) **Prior Publication Data**

US 2012/0220718 A1 Aug. 30, 2012

Related U.S. Application Data

(60) Provisional application No. 61/263,637, filed on Nov.
23, 2009.

(51) **Int. Cl.**
C09D 11/326 (2014.01)

(52) **U.S. Cl.**
CPC **C09D 11/326** (2013.01)

(58) **Field of Classification Search**

CPC C09D 11/326

USPC 523/160

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,479,310	A	11/1969	Bayer et al.	
4,108,814	A	8/1978	Reiff et al.	
4,408,008	A	10/1983	Markusch et al.	
5,085,698	A	2/1992	Ma et al.	
5,990,245	A	11/1999	Esselborn et al.	
6,248,839	B1	6/2001	Esselborn et al.	
6,316,586	B1	11/2001	Sunkara	
8,957,131	B2 *	2/2015	Berge et al.	523/160
2004/0249088	A1	12/2004	Hees et al.	
2005/0027092	A1 *	2/2005	Steidl et al.	528/44
2008/0227945	A1	9/2008	Richards et al.	
2008/0318009	A1	12/2008	Berge et al.	
2009/0259012	A1	10/2009	Roberts	
2009/0281240	A1	11/2009	Li et al.	
2010/0143589	A1 *	6/2010	Spinelli et al.	427/256
2012/0214939	A1 *	8/2012	Li et al.	524/591
2013/0102729	A1 *	4/2013	Li et al.	524/591

OTHER PUBLICATIONS

Corresponding case PCT/US10/57356, International Search Author-
ity/United States, Commissioner for Patents, Alexandria, VA, Autho-
rized Officer Lee W. Young, Jan. 11, 2011.

"C.I." designation for pigments established by Society of Dyers and
Colourists, Bradford, Yorkshire, UK and published in The Color
Index, Third Edition, 1971.

* cited by examiner

Primary Examiner — Vickey Nerangis

(74) *Attorney, Agent, or Firm* — Simon L. Xu

(57) **ABSTRACT**

The present disclosure provides an ink-jet ink comprising an
aqueous ink vehicle and an aqueous dispersion, the aqueous
dispersion comprises a colorant and a polyurethane dispers-
ant, wherein said polyurethane dispersant is comprised of a
polymer having a cross-linkable moiety, wherein the cross-
linkable moiety is cross-linked with a cross-linking agent.

19 Claims, No Drawings

1

INK-JET INK COMPRISING CROSS-LINKED PIGMENT DISPERSION BASED ON POLYURETHANE DISPERSANTS

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Ser. No. 61/263,637, filed Nov. 23, 2009.

BACKGROUND OF THE INVENTION

This disclosure relates to novel aqueous dispersions of colorants and polyurethane dispersants containing cross-

linkable moieties, the cross-linked polyurethane dispersants that produce the stable aqueous colorant dispersions, the process of making same and the use thereof in ink-jet.

Aqueous dispersions of pigment particles are widely used in ink-jet printing. Because a pigment is typically not soluble in an aqueous vehicle, it is often required to use a dispersing agent, such as a polymeric dispersant or a surfactant, to produce a stable dispersion of the pigment in the aqueous vehicle. However, because the pigment is dispersed in a liquid vehicle, there is a tendency for pigment particles to agglomerate or flocculate while the ink is being stored or while the ink is being used, for example, being printed.

There has been effort in the art directed at improving the stability of pigment dispersions. The effort to improve dispersion stability to date has included improvements in the processes used to make the dispersions, the development of new dispersants and the exploration of the interaction between dispersants and pigment particles, and between dispersants and aqueous vehicle. While much of the effort has general application at improving dispersion stability, some of that effort has not found utility in particular applications. For example, the pigment dispersions used in ink-jet printing applications have very unique and demanding requirements. It is critical that ink components comprising pigment dispersion remain stable, not only in storage but also over repeated jetting cycles. It is also desirable that the pigment dispersions offer good durability, good rub-fastness, wet-fastness and highlighter pen fastness.

A need exists for highly stable, higher-quality and different property inks for ink-jet applications. Although improvements in polymeric dispersants have significantly contributed to improved ink-jet inks, the current dispersants still do not provide inks with the requisite stability, durability, optical density and chroma needed for ink-jet applications. The present invention satisfies this need by providing a cross-linked pigment dispersion based on a polyurethane dispersant having cross-linkable moieties both pendent to the polymer backbone and terminal to the polymer chain, and the cross-linking of these moieties with a cross-linking agent.

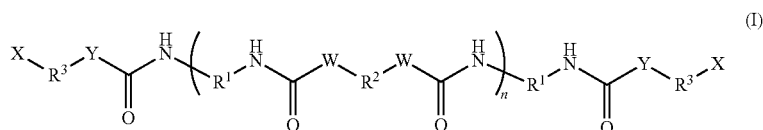
2

SUMMARY OF THE INVENTION

An embodiment of the invention provides an aqueous pigment dispersion comprising a colorant and a polyurethane dispersant, wherein said polyurethane dispersant is comprised of a polymer with:

(a) an aqueous dispersing moiety, and

(b) a cross-linkable moiety that is cross-linked with a cross-linking agent, wherein said cross-linking moiety is pendent to the polymer backbone and terminal to the polymer chain; wherein the polyurethane dispersant comprises at least one compound of the general structure of Formula I:



wherein each X is independently OH, SH, COOH or NHR^4 ;

each Y is independently O, S or NR^4 ;

each W is N, O or S;

each R^1 is independently C_1 - C_{20} alkyl, C_3 - C_{20} substituted alkyl, C_6 - C_{40} aryl or C_9 - C_{40} substituted aryl;

R^2 is comprised of difunctional isocyanate reactants Z^1 , Z^2 and Z^3 , wherein there is at least one at least one Z^2 and at least one Z^3 ;

each R^3 is independently C_1 - C_{20} alkyl or C_3 - C_{20} substituted alkyl;

each R^4 is independently $-\text{R}^3-\text{X}$, H, C_1 - C_{20} alkyl or C_3 - C_{20} substituted alkyl;

n is an integer from 2 to 30;

Z^1 is a difunctional isocyanate reactant substituted with an aqueous dispersing moiety;

Z^2 is a difunctional isocyanate reactant substituted with one or more cross-linkable moieties; and

Z^3 is a polyol with MW less than 3000.

Another embodiment provides that the cross-linking agent is one or members selected from the group consisting of epoxide, isocyanate, carbodiimide, N-methylol, oxazoline, silane, and mixtures thereof.

Another embodiment provides that Z^1 is a poly substituted with the aqueous dispersing moiety.

Another embodiment provides that Z^2 is a polyol substituted with one or more cross-linkable moieties.

Another embodiment provides that the aqueous dispersing moiety consists of one or more carboxyl groups.

Another embodiment provides that the cross-linkable moiety consists of one or more carboxyl groups.

Another embodiment provides that Y is NR^4 .

Another embodiment provides that X is OH.

Another embodiment provides that X is NHR^4 .

Another embodiment provides that R^4 is $-\text{R}^3-\text{X}$.

Another embodiment provides that each W is O.

Another embodiment provides that each W is N.

Another embodiment provides that the mole ratio of the cross-linkable moiety to the cross-linking agent is from 15:1 to 1:1.5.

Another embodiment provides that the mole ratio of the cross-linkable moiety to the cross-linking agent is from 9:1 to 1:1.1.

Another embodiment provides that the mole ratio of the cross-linkable moiety to the cross-linking agent is from 8:1 to 1:1.

Yet another embodiment provides an ink-jet ink comprising an aqueous ink vehicle and an aqueous dispersion, wherein said aqueous dispersion comprises a colorant and a polyurethane dispersant, wherein said polyurethane dispersant is as set forth above.

These and other features and advantages of the present invention will be more readily understood by those of ordinary skill in the art from a reading of the following Detailed Description. Certain features of the invention which are, for clarity, described above and below as a separate embodiment, may also be provided in combination in a single embodiment. Conversely various features of the invention that are described in the context of a single embodiment, may also be provided separately or in any subcombination.

DETAILED DESCRIPTION

Unless otherwise stated or defined, all technical and scientific terms used herein have commonly understood meanings by one of ordinary skill in the art to which this invention pertains.

Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

As used herein, the dispersions produced with the polyurethane described above can be utilized to disperse particles, especially pigments for ink-jet inks. These inks can be printed on all normally used ink-jet substrates including textile substrates.

As used herein, the term "dispersion" means a two phase system where one phase consists of finely divided particles (often in the colloidal size range) distributed throughout a bulk substance, of the particles being the dispersed or internal phase and the bulk substance being the continuous or external phase.

As used herein, the term "dispersant" means a surface active agent added to a suspending medium to promote uniform and maximum separation of extremely fine solid particles often of colloidal size. For pigments, dispersants are most often polymeric dispersants. The polyurethane dispersants described herein are in fact dispersions themselves.

As used herein, the term "OD" means optical density.

As used herein, the term "aqueous vehicle" refers to water or a mixture of water and at least one water-soluble, or partially water-soluble (i.e. methyl ethyl ketone), organic solvent (co-solvent).

As used herein the term "ionizable groups," means potentially ionic groups.

As used herein, the term "substantially" means being of considerable degree, almost all.

As used herein, the term "MW" means weight average molecular weight.

As used herein, the term "D50" means the volume particle diameter of the 50th percentile (median) of the distribution of particle sizes.

As used herein, the term "D95" means the volume particle diameter of the 95th percentile of the distribution of particle sizes.

As used herein, the term "pendent" means that a substituent is directly attached to the backbone of a polymer or via a linkage of 1 to 10 atoms.

As used herein, the term "NCO" means isocyanate.

As used herein, the term "cPs" means centipoise, a viscosity unit.

As used herein, the term "mN·m⁻¹" means milliNewtons per meter, a surface tension unit.

As used herein, the term "mPa·s" means millipascal second, a viscosity unit.

As used herein, the term "prepolymer" means the polymer that is an intermediate in a polymerization process, and can be considered a polymer.

As used herein, the term "AN" means acid number, mg KOH/gram of solid polymer.

As used herein, the term "PUD" means the polyurethanes dispersions described herein.

As used herein, the term "BMEA" means bis(methoxyethylamine).

As used herein, the term "DBTDL" means dibutyltin dilaurate.

As used herein, the term "DEA" means diethanolamine.

As used herein, the term "DMPA" means dimethylol propionic acid.

As used herein, the term "HDI" means 1,6-hexamethylene diisocyanate.

As used herein, the term "IPDI" means isophorone diisocyanate.

As used herein, the term "TMDI" means trimethylhexamethylene diisocyanate.

As used herein, the term "TMXD1" means m-tetramethylene xylene diisocyanate.

As used herein, the term "NMP" means n-Methyl pyrrolidone.

As used herein, the term "TDI" means 2,4-toluene diisocyanate.

As used herein, the term "MDI" means 4,4'-diphenylmethane diisocyanate.

As used herein, the term "H₁₂MDI" means 4,4'-dicyclohexylmethane diisocyanate.

As used herein, the term "TODI" means 3,3'-dimethyl-4,4'-biphenyl diisocyanate.

As used herein, the term "C₁₂DI" means dodecane diisocyanate.

As used herein, the term "NDI" means 1,5-naphthalene diisocyanate.

As used herein, the term "IPDI" means isophorone diisocyanate.

As used herein, the term "TEB" means triethylene glycol monobutyl ether, a reagent supplied by Dow Chemical.

As used herein, the term "Sulfolane" means tetramethylene sulfone.

As used herein, the term "TRB-2" means Dainichiseika® TRB-2, a cyan pigment.

5

As used herein, Terathane® 650 is a polyether diol from Invista, Wichita, Kans.

As used herein, Eternacoll® UH-50 is a polycarbonate diol from UBE Industries, Tokyo, Japan.

As used herein, Denacol® 321 is trimethylolpropane polyglycidyl ether, a cross-linking reagent from Nagase Chemicals Ltd., Osaka, Japan.

As used herein, Denacol® 313 is glycerol polyglycidyl ether, a cross-linking reagent from Nagase Chemicals Ltd., Osaka, Japan.

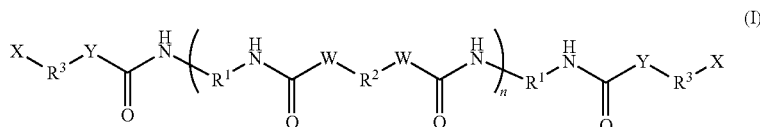
Unless otherwise noted, the above chemicals were obtained from Aldrich (Milwaukee, Wis.) or other similar suppliers of laboratory chemicals.

In addition, references in the singular may also include the plural (for example, "a" and "an" may refer to one, or one or more) unless the context specifically states otherwise.

Polyurethane Dispersants

Polyurethane polymers are, for the purposes of the present disclosure, polymers wherein the polymer backbone contains urethane linkage derived from the reaction of an isocyanate group (from, a di- or higher-functional monomeric, oligomeric or polymeric polyisocyanate) with a hydroxyl group (from, a di- or higher-functional monomeric, oligomeric or polymeric polyol). Such polymers may, in addition to the urethane linkage, also contain other isocyanate-derived linkages such as urea, as well as other types of linkages present in the polyisocyanate components or polyol components (such as, for example, ester and ether linkage).

The polyurethane dispersant of the present invention comprises at least one compound of the general structure of Formula I:



wherein each X is independently OH, SH, COOH or NHR⁴;

each Y is independently O, S or NR⁴;

each W is N, O or S;

each is independently C₁-C₂₀ alkyl, C₃-C₂₀ substituted alkyl, C₆-C₄₀ aryl or C₉-C₄₀ substituted aryl;

R² is comprised of difunctional isocyanate reactants Z¹, Z² and Z³, wherein there is at least one at least one Z² and at least one Z³;

each R³ is independently C₁-C₂₀ alkyl or C₃-C₂₀ substituted alkyl;

each R⁴ is independently —R³—X, H, C₁-C₂₀ alkyl or C₃-C₂₀ substituted alkyl;

n is an integer from 2 to 30;

Z¹ is a functional isocyanate reactant substituted with an aqueous dispersing moiety;

Z² is a difunctional isocyanate reactant substituted with one or more cross-linkable moieties; and

Z³ is a polyol with MW less than 3000.

The key features of the polyurethane dispersant are the cross-linkable moieties that are pendent to the polymer backbone and terminal to the polymer chain. The term "pendent" means that a substituent is directly attached to the backbone of a polymer or via a linkage of between 1 to 10 atoms. Typically, the cross-linkable moieties that are pendent to the polymer backbone reside in the R² group of Formula I. Specifically the Z² component in R² is a polyol substituted with

6

one or more cross-linkable moieties. Typically these cross-linkable moieties are carboxyl, hydroxyl, amino or mecapto groups. The cross-linkable moieties that are terminal to the polymer chain are represented by the X group in Formula I. These cross-linkable, moieties, upon reacting with a cross-linking agent, provide a cross-linked pigment dispersion having superior properties.

The R² group in Formula I is comprised of difunctional isocyanate reactants Z¹, Z² and Z³, wherein there is at least one Z¹, at least one Z² and at least one Z³. This R² group provides the polyurethanes with significant areas of hydrophobic segment which can be effective in dispersing pigments. While not being bound by theory, these areas of hydrophobic segment may be effective as the part of the dispersant that is associated with the pigment surfaces. The polyurethane dispersant must have at least one at least one Z² and at least one Z³ to satisfy the requirements that the polyurethane contains an aqueous dispersing moiety, and cross-linkable moieties both pendent to the polymer backbone and terminal to the polymer chain. The blending of Z² and Z³ in the polyurethane can be in any sequence. In certain circumstances, Z² can be the same as Z¹, and in some other circumstances, Z² can be the same as Z³, as long as there are cross-linkable moieties, as defined above, on Z². Depending on the sequence of addition during the synthesis of the polyurethane, the R² component (combination of Z¹, Z² and Z³) can be random or in blocks.

Difunctional Isocyanate Reactant (Z²) and Polyol (Z³)

Often Z² and Z³ are derived from polyolefins that are available from Shell as KRATON LIQUID L and Mitsubishi Chemical as POLYTAL H. More specifically, Z² and Z³ can

be derived from polyester diols, polycarbonate diols, polyester carbonate diols and polyacrylate diols.

Suitable polyester polyols include reaction products of polyhydric; dihydric alcohols to which trihydric alcohols may optionally be added, and polybasic (typically dibasic) carboxylic acids. Trihydric alcohols are limited to at most about 2 weight % such that some branching can occur but no significant cross-linking would occur, and may be used in cases in which modest branching of the NCO prepolymer or polyurethane is desired. Instead of these polycarboxylic acids, the corresponding carboxylic acid anhydrides, or polycarboxylic acid esters of lower alcohols, or mixtures thereof may be used for preparing the polyesters.

The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic or heterocyclic or mixtures thereof and they may be substituted, for example, by halogen atoms, or unsaturated. The following, are mentioned as examples: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, 1,12-dodecylidic acid, phthalic acid, isophthalic acid, trimellitic acid, phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, tetrachlorophthalic acid anhydride, endomethylene tetrahydrophthalic acid anhydride, glutaric acid anhydride, maleic acid, maleic acid anhydride, fumaric acid, dimeric and trimeric fatty acids such as oleic acid, which may be mixed with monomeric fatty acids, dimethyl terephthalates and bis-glycol terephthalate.

Typically, polyester diols can be blended with hydroxyl terminated polybutylene adipate), polybutylene succinate), polyethylene adipate), poly(1,2-propylene adipate), poly(trimethylene adipate), poly(trimethylene succinate), polylactic acid ester diol and polycaprolactone diol. Other hydroxyl terminated polyester diols are copolyethers comprising, repeat units derived from a diol and a sulfonated dicarboxylic acid and prepared as described in U.S. Pat. No. 6,316,586.

Polycarbonates containing hydroxyl groups include those known, such as the products obtained from the reaction of diols such as propanediol-(1,3), butanediol-(1,4) or hexanediol-(1,6), diethylene glycol, triethylene glycol or tetraethylene glycol, and higher polyether diols with phosgene, diarylcarbonates such as diphenylcarbonate, dialkylcarbonates such as diethylcarbonate, or with cyclic carbonates such as ethylene or propylene carbonate. Also suitable are polyester carbonates obtained from the above-mentioned polyesters or polylactones with phosgene, diaryl carbonates, dialkyl carbonates or cyclic carbonates.

Polycarbonate diols for blending are optionally selected from the group consisting of polyethylene carbonate diol, polytrimethylene carbonate diol, polybutylene carbonate diol and polyhexylene carbonate.

Poly(meth)acrylates containing hydroxyl groups include those common in the art of addition polymerization such as cationic, anionic and radical polymerization and the like. Examples are alpha-omega diols. An example of these type of diols are those which are prepared by a "living" or "control" or chain transfer polymerization processes which enables the placement of one hydroxyl group at or near the termini of the polymer. For further examples of making these diols, see: U.S. Pat. Nos. 6,248,839 and 5,990,245.

The MW for the polyols described above is typically less than 5000. Typically the MW for Z^3 (a polyol) is less than 3000.

Difunctional Isocyanate Reactant (Z^1)

The difunctional isocyanate reactant Z^1 in Formula I contains an aqueous dispersing moiety that is ionic or ionizable. In the context of this disclosure, the term "isocyanate reactant", or "isocyanate reactive", is taken to include groups well known to those of ordinary skill in the relevant art to react with isocyanates, and typically include hydroxyl, primary amino and secondary amino groups. The term "difunctional" means containing two of the isocyanate reactive groups.

Examples of ionic dispersing groups include carboxylate groups ($-\text{COOM}$), phosphate groups ($-\text{OPO}_3\text{M}_2$), phosphonate groups ($-\text{PO}_3\text{M}_2$), sulfonate groups ($-\text{SO}_3\text{M}$), and quaternary ammonium groups ($-\text{NR}_3\text{Q}$), wherein M is a cation such as a monovalent metal ion (e.g., Na^+ , K^+ , Li^+ , etc.), H^+ or NR_4^+ ; Q is a monovalent anion such as chloride or hydroxide; and each R can independently be an alkyl, aralkyl, aryl or hydrogen. These ionic dispersing groups are typically located pendent to the polyurethane backbone.

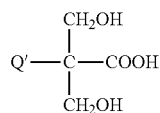
The ionizable groups in general correspond to the ionic groups, except that they are in the acid (such as carboxyl $-\text{COOH}$) or base (such as primary, secondary or tertiary amine $-\text{NH}_2$, $-\text{NRH}$, or $-\text{NR}_2$) form. The ionizable groups are such that they are readily converted to their ionic form during the dispersion/polymer preparation process as discussed below.

With respect to compounds which contain isocyanate reactive groups and ionic or potentially ionic groups, the isocyanate reactive groups are typically amino and hydroxyl groups. The potentially ionic groups or their corresponding ionic groups may be cationic or anionic, although the anionic groups are preferred. Specific examples of anionic groups

include carboxylate and sulfonate groups. Examples of cationic groups include quaternary ammonium groups and sulfonium groups.

In the case of anionic group substitution, the groups can be carboxylic acid groups, carboxylate groups, sulphonic acid groups, sulphonate groups, phosphoric acid groups and phosphonate groups. The acid salts are formed by neutralizing the corresponding acid groups either prior to, during or after formation of the NCO prepolymer.

Suitable compounds for incorporating carboxyl groups are described in U.S. Pat. Nos. 3,479,310, 4,108,814 and 4,408,008. Examples of carboxylic group-containing compounds are the hydroxy-carboxylic acids corresponding to the formula $(\text{HO})_p\text{Q}(\text{COOH})_q$, wherein Q is C_1 - C_{10} alkyl, p is 1 or 2, and q is 1 to 3. Examples of these hydroxy-carboxylic acids include citric acid, tartaric acid and hydroxypivalic acid. Optional dihydroxy alkanolic acids include the α,α -dimethylol alkanolic acids represented by the structure of Formula II below:



wherein Q' is hydrogen or C_1 - C_8 alkyl. Additional α,α -dimethylol alkanolic acids are represented by the structural formula $\text{R}^5\text{C}-(\text{CH}_2\text{OH})_2-\text{COOH}$, wherein R^5 is hydrogen or C_1 - C_8 alkyl. Examples of these ionizable diols include, but are not limited to, dimethylolacetic acid, 2,2'-dimethylolbutanoic acid, 2,2'-dimethylolpropionic acid (DMPA), and 2,2'-dimethylolbutyric acid. Suitable carboxylates also include $\text{H}_2\text{N}-(\text{CH}_2)_4-\text{CH}(\text{CO}_2\text{H})-\text{NH}_2$, and $\text{H}_2\text{N}-\text{CH}_2-\text{CH}-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{Na}$.

Typical sulfonate groups for incorporation into the polyurethanes include diol sulfonates described in U.S. Pat. No. 4,108,814. Suitable diol sulfonate compounds also include hydroxyl terminated copolyethers comprising repeat units derived from the reaction of a diol and a sulfonated dicarboxylic acid. Specifically, the sulfonated dicarboxylic acid is 5-sulfo-isophthalic acid and the diol is 1,3-propanediol. Other suitable sulfonates include the ones represented by formula $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-(\text{CH}_2)_r-\text{SO}_3\text{Na}$, wherein r is 2 or 3.

When the ionic stabilizing groups are acids, the acid groups are incorporated in an amount sufficient to provide an acid group content for the polyurethane, known by those skilled in the art as acid number (mg KOH per gram solid polymer), of at least 6, typically at least 10, and even more typically 20 milligrams KOH per 1.0 gram of polyurethane. The upper limit for the acid number (AN) is about 120, and typically about 100.

Within the context of this disclosure. The term "neutralizing agents" is meant to embrace all types of agents which are useful for converting potentially ionic or ionizable groups to ionic groups. When amines are used as the neutralizing agent, the chain terminating reaction producing the urea termination is typically completed prior to the addition of the neutralizing agent that can also act as an isocyanate reactive group.

In order to convert an anionic group to its salt form before, during or after its incorporation into a prepolymer, either volatile or nonvolatile basic materials may be used to form the counterion of the anionic group. Volatile bases are those wherein at least about 90% of the base used to form the

counterion of the anionic group volatilizes under the conditions used to remove water from the aqueous polyurethane dispersions. Nonvolatile bases are those wherein at least about 90 of the base does not volatilize under the conditions used to remove water from the aqueous polyurethane dispersions.

Suitable volatile basic organic compounds for neutralizing the potential anionic groups are the primary, secondary or tertiary amines. Examples of these amines are trimethyl amine, triethyl amine, triisopropyl amine, tributyl amine, N,N-dimethylcyclohexyl amine, N,N-dimethylstearyl amine, N,N-dimethylaniline, N-methylmorpholine, N-ethylmorpholine, N-methylpiperazine, N-methylpyrrolidine, N-methylpiperidine, N,N-dimethylethanol amine, N,N-diethyl-ethanol amine, triethanolamine, N-methyldiethanol amine, dimethylaminopropanol, 2-methoxyethyldimethyl amine, N-hydroxyethylpiperazine, 2-(2-dimethylaminoethoxy)-ethanol and 5-diethylamino-2-pentanone.

Suitable nonvolatile bases include alkoxides, hydroxides, carbonates or bicarbonates of monovalent metals, especially the alkali metals, lithium, sodium and potassium.

When the anionic groups on the polyurethane are neutralized, they provide hydrophilicity to the polymer and better enable it to stably disperse pigment in water. However, it may be desirable to control the degree of neutralization. When the anionic groups on the polyurethane are partially neutralized, the polyurethane becomes more hydrophobic and therefore adsorbs onto the pigment surface. Reducing the amount of the un-adsorbed polymer from the pigment dispersion provides an advantageous condition for the cross-linkable moieties on the polyurethane, adsorbing onto the pigment surface, to react with a cross-linking agent without the competition from cross-linkable moieties on the un-adsorbed polyurethane. Typically the degree of neutralization is from 40% to 100%, and more typically from 50% to 70%, depending on the acid number of the polyurethane.

Capping of the Polyurethane

The capping agent for terminating the polyurethane chain is usually a primary or secondary amine, an alcohol, or a mercapto. In Formula I, the capping agent is shown as a substituent on the polyurethane.

The amount of capping agent employed should be approximately equivalent to the free isocyanate groups in the prepolymer. The ratio of active hydrogens from amine in the capping agent to isocyanate groups in the prepolymer is in the range of from about 1.0:1.0 to about 3.0:1.0, more typically from about 1.0:1.0 to about 1.5:1.0, and still more typically from about 1.0:1.0 to about 1.05:1, on an equivalent basis. Although any isocyanate groups that are not terminated with an amine can react with other isocyanate reactive functional group or water, the ratios of capping agent to isocyanate group is chosen to ensure a urea termination. Amine termination of the polyurethane is avoided by the choice and amount of capping agent leading to a urea terminated polyurethane. This results in better molecular weight control and better properties when used as a particle dispersant, and ease in handling when added to formulations.

Any primary or secondary amines substituted with reactive isocyanate groups may be used as chain terminators. Especially useful are aliphatic primary or secondary monoamines, or diamines. Less reactive isocyanate groups such as hydroxyl, carboxyl, and mercapto could also be used. Example of amines useful as chain terminators include, but are not restricted to, diethanolamine, monoethanolamine, 3-amino-1-propanol, isopropanolamine, N-ethylethanolamine, diisopropanolamine, 6-aminocaproic acid, 8-aminocaprylic acid, and 3-aminoadipic acid. An typical isocyanate

reactive chain terminator is diethanolamine. The hydroxyl functionalities on diethanolamine serve as cross-linking moieties terminal to the polyurethane chain.

Polyisocyanate Component

Suitable polyisocyanates are those that contain either aromatic, cycloaliphatic or aliphatic groups bound to the isocyanate groups. Mixtures of these compounds may also be used. If aromatic isocyanates are used, cycloaliphatic or aliphatic isocyanates can be present as well.

Any diisocyanate useful in preparing polyurethanes via its reaction with polyether glycols, diols or amines can be used in this invention.

Examples of suitable diisocyanates include, but are not limited to, 2,4-toluene diisocyanate (TDI), 2,6-toluene diisocyanate, trimethyl hexamethylene diisocyanate (TMDI), 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI), 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI), dodecane diisocyanate (C₁₂DI), m-tetramethylene xylylene diisocyanate (TMXDI), 1,4-benzene diisocyanate, trans-cyclohexane-1,4-diisocyanate, 1,5-naphthalene diisocyanate (NDI), 1,6-hexamethylene diisocyanate (HDI), 4,6-xylylene diisocyanate, isophorone diisocyanate (IPDI), and combinations thereof.

Small amounts, typically less than about 3% by weight based on the weight of the diisocyanate, of monoisocyanates or polyisocyanates can be used in a mixture with the diisocyanate. Examples of useful monoisocyanates include alkyl isocyanates such as octadecyl isocyanate and aryl isocyanates such as phenyl isocyanate. Examples of useful polyisocyanates are triisocyanatotoluene HDI trimer and polymeric MDI.

Cross-Linking of Dispersant

The polyurethane dispersants have cross-linkable functional moieties both pendent to the polymer backbone and terminal to the polymer chain. The dispersants are thus capable of reacting with a cross-linking compound. Identified in the table below are suitable cross-linkable functional groups that are in the polymeric dispersant and the companion cross-linking groups that may be present in the cross-linking compound.

Cross-linkable Moieties	Cross-linking Groups
COOH	Epoxide, Carbodiimide, Oxazoline, N-Methyl
Hydroxyl	Epoxide, Silane, Isocyanate, N-Methyl
Amino	Epoxide, Carbodiimide, Oxazoline, N-Methyl

The cross-linkable moieties can be situated at the terminals of the polymer chain (group X in Formula I) or be incorporated into the R² group (in Formula I) of the polyurethane dispersant by selection of appropriate Z². Mixtures of these cross-linkable moieties may also be present in the polyurethane dispersant. Useful cross-linking compounds are those which are soluble or insoluble in the aqueous vehicle, including m-tetramethylene diisocyanate (TMXDI), isophorone diisocyanate (IPDI), trimethylpropane polyglycidyl ether, polyglycerol polyglycidyl ether, oxazoline-functional polymers, waterborne polycarbodiimide resin, and silane.

The mole ratio of the cross-linkable moiety on the polymer chain to the cross-linking groups on the cross-linking agent is from 15:1 to 1:1.5, typically from 9:1 to 1:1.1, and most typically from 8:1 to 1:1. In calculating the mole ratio, all cross-linkable moieties on the polymer chain and all cross-linking groups on the cross-linking agent are included

Colorants

A wide variety of organic pigments, alone or in combination, may be dispersed with the polyurethane dispersant to prepare an ink, especially an ink-jet ink. The term "pigment" as used herein means an insoluble colorant that requires to be dispersed with a dispersant and processed under dispersive conditions in the presence of a dispersant. The colorant also includes dispersed dyes. The dispersion process results in a stable dispersed pigment. The pigment used with the inventive polyurethane dispersants does not include self-dispersed pigments. The pigment particles are sufficiently small to permit free flow of the ink through the ink-jet printing device, especially at the ejecting nozzles that usually have a diameter ranging from about 10 micron to about 50 micron. The particle size also has an influence on the pigment dispersion stability, which is critical throughout the life of the ink. Brownian motion of minute particles will help prevent the particles from flocculation. It is also desirable to use small particles for maximum color strength and gloss. The range of useful particle size is typically about 0.005 micron to about 15 micron. Typically, the pigment particle size should range from about 0.005 to about 5 micron and, most typically, from about 0.005 to about 1 micron. The average particle size as measured by dynamic light scattering is less than about 500 nm, typically less than about 300 nm.

The selected pigment(s) may be used in dry or wet form. For example, pigments are usually manufactured in aqueous media, and the resulting pigments are obtained as a water-wet presscake. In a presscake form, the pigment does not agglomerate to the extent like it is in dry form. Thus, pigments in water-wet presscake form do not require as much mixing energy to de-agglomerate in the premix process as pigments in dry form. Representative commercial dry pigments are listed in U.S. Pat. No. 5,085,698.

Some examples of pigments with coloristic properties useful in inkjet inks include: cyan pigments from Pigment Blue 15:3 and Pigment Blue 15:4; magenta pigments from Pigment Red 122 and Pigment Red 202; yellow pigments from Pigment Yellow 14, Pigment Yellow 95, Pigment Yellow 110, Pigment Yellow 114, Pigment Yellow 128 and Pigment Yellow 155; red pigments from Pigment Orange 5, Pigment Orange 34, Pigment Orange 43, Pigment Orange 62, Pigment Red 17, Pigment Red 49:2, Pigment Red 112, Pigment Red 149, Pigment Red 177, Pigment Red 178, Pigment Red 188, Pigment Red 255 and Pigment Red 264; green pigments from Pigment Green Pigment Green 2, Pigment Green 7 and Pigment Green 36; blue pigments from Pigment Blue 60, Pigment Violet 3, Pigment Violet 19, Pigment Violet 23, Pigment Violet 32, Pigment Violet 36 and Pigment Violet 38; white pigments such as TiO_2 and ZnO ; and black pigment carbon black. The pigment names and abbreviations used herein are the "C.I." designation for pigments established by Society of Dyers and Colourists, Bradford, Yorkshire, UK and published in *The Color Index*, Third Edition, 1971.

In the case of organic pigments, the ink may contain up to approximately 30%, typically from 0.1% to about 25%, and more specifically from 0.25% to 10% of pigment, by weight based on the total ink weight. If an inorganic pigment is selected, the ink will tend to contain higher percentages by weight of pigment than with comparable inks employing organic pigment, since inorganic pigments generally have higher densities than organic pigments.

The polyurethane polymer dispersant is typically present in the range of from 0.1% to 20%, and more specifically from 0.2 to about 10%, by weight based on the weight of the total ink composition.

Preparation of Polyurethane Dispersant

The polyurethane dispersants of the present invention can be prepared by a one-step mixing or a stepwise method. The physical form of the polyurethane prior to its use as a dispersant is an aqueous dispersion. In the one-step mixing process, isocyanate terminated polyurethane is prepared by mixing Z^2 and Z^3 in a solvent, followed by adding a diisocyanate to the mixture. This reaction is conducted at from about 40° C. to about 100° C., and typically from about 50° C. to about 90° C. The ratio of isocyanate to isocyanate reactive groups (Z^1 , Z^2 and Z^3) is from about 1.3:1 to about 1.05:1, and more typically from about 1.25:1 to about 1.1:1. When the targeted percentage of isocyanate content is reached, a primary or secondary amine capping agent is added. The polyurethane solution is then converted to an aqueous dispersion via the addition of de-ionized water under a high shearing operation. Volatile solvent(s), if present, are distilled under reduced pressure.

The NCO-functional prepolymers should be substantially linear, and this may be achieved by maintaining the average functionality of the prepolymer starting components at or below 2:1.

In the stepwise method, a polyurethane is prepared by dissolving the Z^1 reactant in a solvent, followed by adding a diisocyanate to the mixture. Once the initial percentage of isocyanate content target is reached, the Z^2 and Z^3 components are added. This reaction is conducted at from about 40° C. to about 100° C., and typically from about 50° C. to about 90° C. The typical ratio of isocyanate to isocyanate reactive groups is from about 1.3:1 to about 1.05:1, and more typically from about 1.25:1 to about 1.1:1. Alternately, the Z^2 and reactants may be reacted in the first step, and the Z^1 reactant may be added after the initial percentage of isocyanate content target is reached. When the final targeted percentage of isocyanate content is reached, a capping agent is added. The polyurethane solution is then converted to an aqueous polyurethane dispersion via the addition of water under a high shearing operation. Volatile solvent(s), if present, are distilled under reduced pressure.

Catalysts are not necessary for the preparation of the polyurethanes, but may provide advantages in a large scale manufacturing process. The catalysts most widely used are tertiary amines and organo-tin compounds such as stannous octoate, dibutyltin dioctoate and dibutyltin dilaurate.

Preparation of the polyurethane for subsequent conversion to a dispersion is facilitated by using a solvent. Suitable solvents are those that are miscible with water and inert to isocyanates and other reactants utilized in forming the polyurethanes. If it is desired to prepare a solvent-free dispersion, the solvent used should have sufficient volatility to allow its removal by distillation. Typical solvents useful in the practice of the present invention are acetone, methyl ethyl ketone, toluene, and N-methyl pyrrolidone. Alternatively, the polyurethane can be prepared in a melt with less than 5% of solvent.

Mixtures of compounds or polymers having mixed NCO reactive groups can also be used in the preparation of the polyurethane of the present invention.

Processing conditions for preparing the NCO containing prepolymers are well known to one skilled in the art. The finished NCO-containing prepolymer should have an isocyanate content of from about 1 to about 20%, typically from about 1 to about 10% by weight, based on the weight of prepolymer solids.

As described above, a sufficient amount of the ionic groups must be neutralized so that the result in polyurethane can have a proper balance of hydrophilicity and hydrophobicity. Typi-

cally the degree of neutralization is from 40% to 100%, and more typically from 50 to 70%, depending on the acid number of the polyurethane.

Suitable neutralizing agents for converting the acid groups to salt groups include tertiary amines, alkali metal cations and ammonia. Neutralizing agents can be trialkyl-substituted tertiary amines, such as triethyl amine, tripropyl amine, dimethylcyclohexyl amine, dimethylethanol amine, and triethanol amine and dimethylethyl amine. Substituted amines such as diethyl ethanol amine or diethanol methyl amine are also useful neutralizing agents.

Neutralization may take place at any point in the process. Typical procedures include at least some neutralization of the prepolymer, which is then chain extended/terminated in water in the presence of additional neutralizing agent.

The capping agent for terminating the polyurethane chain is usually a primary or secondary amine, an alcohol, or a mecapto. The amount of capping agent employed should be approximately equivalent to the free isocyanate groups in the prepolymer. The ratio of active hydrogens from amine in the capping agent to isocyanate groups in the prepolymer is in the range of from about 1.0:1.0 to about 3.0:1.0, more typically from about 1.0:1.0 to about 1.5:1.0, and still more typically from about 1.0:1.0 to about 1.05:1, on an equivalent basis.

Conversion of the polyurethane obtained from the methods described above to an aqueous dispersion is completed by addition of de-ionized water. If desired, solvent can then be removed partially or substantially by distillation under reduced pressure. The final product is a stable, aqueous polyurethane dispersion having a solids content of up to about 60% by weight, typically from about 10% to about 60% by weight, and more typically from about 20% to about 45% by weight. However, it is always possible to dilute the dispersions to any minimum solids content desired. The solids content of the resulting dispersion may be determined by drying the sample in an oven at 150° C. for 2 hours and comparing the weights before and after drying. The particle size is generally below about 1.0 micron, and typically between about 0.01 to about 0.5 micron. The average particle size should be less than about 0.5 micron, and typically between about 0.01 to about 0.3 micron. The small particle size enhances the stability of the dispersed particles.

Preparation of Pigmented Dispersions

The pigmented dispersions used in this invention can be prepared using any conventional milling process known in the art. Most milling processes use a two-step process involving a first mixing step followed by a second grinding step. The first step comprises mixing of all the ingredients, that is, pigment, dispersants, liquid carriers, neutralizing agent and any optional additives to provide a blended "premix". Typically all liquid ingredients are added first, followed by the dispersants, and lastly the pigment. Mixing is generally done in a stirred mixing vessel, and a high-speed disperser (HSD) is particularly suitable for the mixing step. A Cowels type blade attached to the HSD and operated at from 500 rpm to 4000 rpm, and more typically from 2000 rpm to 3500 rpm, provides optimal shear to achieve the desired mixing. Adequate mixing is usually achieved after mixing under the conditions described above for a period of from 15 to 120 minutes.

The second step comprises grinding of the premix to produce a pigmented dispersion. Typically, grinding involves a media milling process, although other milling techniques can also be used. In the present invention, a lab-scale Eiger Minmill (Model M250, VSE EXP) manufactured by Eiger Machinery Inc., Chicago, Ill. is employed. Grinding was accomplished by charging about 820 grams of 0.5 YTZ®

zirconia media to the mill. The mill disk is operated at a speed between 2000 rpm and 4000 rpm, and typically between 3000 rpm and 3500 rpm. The dispersion is processed using a recirculation grinding process with a typical flow rate through the mill at between 200 to 500 grains/minute, and more typically at 300 grams/minute. The milling may be done using a staged procedure in which a fraction of the solvent is held out of the grind and added after milling is completed. This is done to achieve optimal rheology that maximizes grinding efficiency. The amount of solvent held out during milling varies by dispersion, and is typically between 200 to 400 grams for a batch size with a total of 800 grams. Typically, the dispersions of the present invention are subjected to a total of 4 hours of milling.

For black dispersions, an alternate milling process using a Microfluidizer can be used. Microfluidization is a non-media milling process in which milling is done by pigment impingement through nozzles under high pressures. Typically, pigment dispersions are processed at 15,000 psi with a flow rate of 4.00 grams/minute for a total of 12 passes through the mill. In making the black dispersions in the Examples, a lab-scale (Model M-1107Y, available from Microfluidics of Newton, Mass.) high pressure pneumatic Microfluidizer with a diamond Z. Chamber was employed.

Fillers, plasticizers, pigments, carbon black, silica sols, other polymer dispersions and the known leveling agents, wetting agents, antifoaming agents, stabilizers, and other additives known for the desired end use, may also be incorporated into the dispersions.

Preparation of Cross-linked Pigment Dispersion

In the cross-linking step, a cross-linking compound is mixed with the pigmented dispersions prepared above at room temperature or elevated temperature for a period from 6 h to 8 h. To facilitate the cross-linking reaction, it may be desirable to add a catalyst. Useful catalysts can be those that are either soluble or insoluble in the liquid and can be selected depending upon the crosslinking reactions. Some suitable catalysts include dibutyltin dilaurate (DBTDL), tributyl amine ("TBA") and dimethyldodecyl amine. After the cross-linking reaction is completed, the pH of the cross-linked dispersion can be adjusted to at least about 8.0, more typically to between 8.0 and 12.0, and most typically between 8.0 and 11.0, if needed. Optionally, the dispersion may be further processed using conventional filtration procedures known in the art. The dispersions may be processed using ultrafiltration techniques that remove co-solvents and other contaminants, ions or impurities from the dispersion. Each dispersion can be then tested for pH, conductivity, viscosity and particle size. Dispersion stability is deemed important to demonstrating the utility of the dispersant employed.

Fillers, plasticizers, pigments, carbon black, silica sols, other polymer dispersions and the known leveling agents wetting agents, antifoaming agents, stabilizers, and other additives known for the desired end use, may also be incorporated into the dispersions.

Ink Vehicle

The pigmented ink of this disclosure comprises an ink vehicle typically an aqueous ink vehicle also known as an aqueous carrier medium, the aqueous dispersion and optionally other ingredients.

The ink vehicle is the liquid carrier (or medium) for the aqueous dispersion(s) and optional additives. The term "aqueous ink vehicle" refers to an ink vehicle comprised of water or a mixture of water and one or more organic, water-soluble vehicle components commonly referred to as co-solvents or humectants. Selection of a suitable mixture depends on requirements of the specific application, such as

desired surface tension and viscosity, the selected pigment, drying time of the pigmented ink jet ink, and the type of paper onto which the ink will be printed. Sometimes in the art, when a co-solvent can assist in the penetration and drying of an ink on a printed substrate, it is referred to as a penetrant.

Examples of water-soluble organic solvents and humectants include: alcohols, ketones, keto-alcohols, ethers and others, such as thiodiglycol, Sulfolane, 2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone and caprolactam; glycols such as ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, dipropylene glycol, trimethylene butylene glycol and hexylene glycol; addition polymers of oxyethylene or oxypropylene such as polyethylene glycol, polypropylene glycol and the like; triols such as glycerol and 1,2,6-hexanetriol; lower alkyl ethers of polyhydric alcohols, such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl, diethylene glycol monoethyl ether; lower dialkyl ethers of polyhydric alcohols, such as diethylene glycol dimethyl or diethyl ether; urea and substituted ureas.

A mixture of water and a polyhydric alcohol, such as diethylene glycol, is typical as the aqueous ink vehicle. In the case of a mixture of water and diethylene glycol, the ink vehicle usually contains from 30% water and 70% diethylene glycol to 95% water and 5% diethylene glycol, more typically from 60% water and 40% diethylene glycol to 95% water and 5% diethylene glycol. Percentages are based on the total weight of the ink vehicle. A mixture of water and butyl carbitol is also an effective ink vehicle.

The amount of ink vehicle in the ink is typically in the range of from 70% to 99.8%, and more typically from 80% to 99.8%, by weight based on total weight of the ink.

The ink vehicle can be made to be fast penetrating (rapid drying) by including surfactants or penetrating agents such as glycol ethers and 1,2-alkanediols. Glycol ethers include ethylene glycol monobutyl ether, diethylene glycol mono-n-propyl ether, ethylene glycol mono-iso-propyl ether, diethylene glycol mono-iso-propyl ether, ethylene glycol mono-n-butyl ether, ethylene glycol mono-t-butyl ether, diethylene glycol mono-n-butyl ether, triethylene glycol mono-n-butyl ether, diethylene glycol mono-t-butyl ether, 1-methyl-1-methoxybutanol, propylene glycol mono-t-butyl ether, propylene glycol mono-n-propyl ether, propylene glycol mono-iso-propyl ether, propylene glycol mono-n-butyl ether, dipropylene glycol mono-n-butyl ether, dipropylene glycol mono-n-propyl ether, and dipropylene glycol mono-isopropyl ether. Typical 1,2-alkanediols are C₄-C₆ alkanediols with 1,2-hexanediol being most typical. Suitable surfactants include ethoxylated acetylene diols (e.g. Surfynol® series commercially available from Air Products), ethoxylated alkyl primary alcohols (e.g. Neodol® series commercially available from Shell) and secondary alcohols (e.g. Tergitol® series commercially available from Union Carbide), sulfosuccinates (e.g. Aerosol® series commercially available from Cytec), organosilicones (e.g. Silwet® series commercially available from Witco and fluoro surfactants (e.g. Zonyl series commercially available from DuPont).

The amount of glycol ether(s) and 1,2-alkanediol(s) added is typically in the range of from 1% to 15%, and more typically from 2% to 10% by weight, based on the total weight of the ink. Surfactants may be used, typically in the amount of from 0.01% to 5% and more typically from 0.2% to 2%, by weight based on the total weight of the ink.

Biocides may be used to inhibit growth of microorganisms.

Pigmented ink jet inks typically have a surface tension in the range of about 20 mN·m⁻¹ to about 70 mN·m⁻¹, at 25° C.

Viscosity can be as high as 30 mPa·s at 25° C., but is typically somewhat lower. The ink has physical properties compatible with a wide range of ejecting conditions, materials construction and the shape and size of the nozzle. The inks should have excellent storage stability for long periods so as not to clog to a significant extent in an ink jet apparatus. Further, the ink should not corrode parts of the ink jet printing device it comes in contact with, and it should be essentially odorless and non-toxic.

Although not restricted to any particular viscosity range or printhead, the inks of the disclosure are particularly suited to lower viscosity applications. Thus the viscosity (at 25° C.) of the inks of this disclosure may be less than about 7 mPa·s, or less than about 5 mPa·s, and even more advantageously, less than about 3.5 mPa·s.

The following examples illustrate the invention without, however, being limited thereto.

EXAMPLES

Extent of Polyurethane Reaction

The extent of polyurethane reaction was determined by a titration with dibutylamine to detect the isocyanate content (NCO %), a common method used in urethane chemistry.

In this method, a sample of the isocyanate containing prepolymer is reacted with a known amount of dibutylamine solution, and the residual amine is back titrated with aqueous HCl.

Particle Size Measurements

The particle size for the polyurethane dispersions, pigments and the inks were determined by dynamic light scattering using a Microtrac® UFA 150 analyzer from Honeywell/Microtrac (Montgomeryville Pa.).

This technique is based on the relationship between the velocity distribution of the particles and the particle size. Laser generated light is scattered from each particle and is Doppler shifted by the particle Brownian motion. The frequency difference between the shifted light and the unshifted light is amplified, digitalized and analyzed to derive the particle size distribution. Results are reported as D50 and D95.

Solid Content Measurement
Solid content for the solvent free polyurethane dispersions was measured with a moisture analyzer, Model MA50 from Sartorius. For polyurethane dispersions containing a high boiling solvent, such as NMP, tetraethylene glycol dimethyl ether, or sulfolane, the solid content was determined by the weight difference before and after baking in an oven set at 150° C. oven for 180 minutes.

Preparation of Polyurethane Dispersants

A total of four polyurethane dispersants as listed in Table 1 below were prepared. These dispersants were later used for preparing pigmented dispersions and cross-linked pigment dispersions.

TABLE 1

Dispersant #	Polyurethane Structure	Acid Number (mg KOH/g solids)
Dispersant 1	DEA Terminated TMXDI/Terathane650	60
Dispersant 2	DEA Terminated TMXDI/Terathane650	80
Dispersant 3	DEA Terminated IPDI/Terathane650	60
Dispersant 4	BMEA Terminated TMXDI/UH-50	55

17

Polyurethane Dispersant 1 (DEA Terminated TMXDI/Terathane650)

To a dry, alkali- and acid-free flask equipped with an additional funnel, a condenser and a stirrer, under a nitrogen atmosphere was added Terathane® 650 (135 g), DMPA (54 g), Sulfolane (132 g) and DBTL (0.06 g). The resulting mixture was heated to 60° C. and thoroughly mixed. To this mixture was added TMXDI (164 g) via the additional funnel followed by rinsing any residual TMXDI in the additional funnel into the flask with Sulfolane (15 g). The temperature for the reaction mixture was raised to 100° C.; and maintained at 100° C. until the isocyanate content reached 1.3% or below. The temperature was then cooled to 60° C. and maintained at 60° C. while DEA (129 g) was added via the additional funnel mounted on the flask over a period of 5 minutes followed by rinsing the residual DEA in the additional funnel into the flask with Sulfolane (5 g). After holding the temperature for 1 hr at 60° C., aqueous KOH (376 g, 3% by weight) was added over a period of 10 minutes via the additional funnel followed by de-ionized water (570 g). The mixture was maintained at 60° C. for 1 hr and cooled to room temperature to provide a polyurethane dispersant with 24% of solids.

Polyurethane Dispersant 2 (DEA Terminated TMXDI/Terathane650)

To a dry, alkali- and acid-free flask equipped with an additional funnel, a condenser and a stirrer, under a nitrogen atmosphere was added Terathane® 650 (100 g), DMPA (70 g), Sulfolane (1.30 g) and DBTL (0.06 g). The resulting mixture was heated to 60° C. and thoroughly mixed. To this mixture was added TMXDI (182 g) via the additional funnel mounted on the flask followed by rinsing any residual TMXDI in the additional funnel into the flask with Sulfolane (15 g). The temperature for the reaction mixture was raised to 100° C. and maintained at 100° C. until the isocyanate content reached 1.3% or below. The temperature was then cooled to 60° C. and maintained at 60° C. while DEA (14.6 g) was added via the additional funnel over a period of 5 minutes followed by rinsing the residual DEA in the additional funnel into the flask with Sulfolane (5 g). After holding the temperature for 1 hr at 60° C., aqueous KOH (487.5 g, 3% by weight) was added over a period of 10 minutes via the additional funnel followed by de-ionized water (461 g). The mixture was maintained at 60° C. for 1 hr and cooled to room temperature to provide a polyurethane dispersant with 22% of solids.

Polyurethane Dispersant 3 (DEA Terminated IPDI/Terathane650)

To a dry, alkali- and acid-free flask equipped with an additional funnel, a condenser and a stirrer, under a nitrogen atmosphere was added Terathane® 650 (155 g), DMPA (54 g), Sulfolane (237 g) and DBTL (0.06 g). The resulting mixture was heated to 60° C. and thoroughly mixed. To this mixture was added IDPI (157 g) via the additional funnel mounted on the flask followed by rinsing any residual IDPI in the additional funnel into the flask with Sulfolane (15 g). The temperature for the reaction mixture was raised to 85° C. and maintained at 85° C. until the isocyanate content reached 1.2% or below. The temperature was then cooled to 60° C. and maintained, at 60+ C. while DEA (13.8 g) was added via the additional funnel over a period of 5 minutes followed by rinsing the residual DEA in the additional funnel into the flask with Sulfolane (5 g). After holding the temperature for 1 hr at 60° C., aqueous KOH (526.5 g, 3% by weight) was added over a period of 10 minutes via the additional funnel followed by de-ionized water (356 g). The mixture was maintained at 60° C. for 1 hr and cooled to room temperature to provide a polyurethane dispersant with 20.16% of solids.

18

Polyurethane Dispersant 4 (BMEA Terminated TMXDI/UH-50)

To a dry, alkali- and acid-free, 2 liter flask equipped with an additional funnel, a condenser and a stirrer, under a nitrogen atmosphere was added Eternacoll® UH-50 (351.1 g), DMPA (261.0 g) and Sulfolane (663.8 g). The contents were heated to 115° C. and mixed under a nitrogen gas purge for 30 minutes. The temperature was then lowered to 60° C. and DBTL (0.08 g) was added followed by TMXDI (713.6 g) via the addition funnel mounted to the flask. The residual TMXDI in the additional funnel was rinsed into the flask with Sulfolane (48.2 g). The stirred reaction mass was allowed to exotherm to 123° C. When exotherm began to slow, the temperature was maintained at 102° C. while monitoring the isocyanate content until it reached 1.01%. Additional Sulfolane (209.7 g) was added to the reactor, and the temperature was lowered to 85.6° C. To the flask was added BMEA (68.88 g) via the additional funnel followed by rinsing the residual BMEA in additional funnel into the flask with Sulfolane (15.24 g). The mixture was maintained at 85.3° C.; for 90 minutes and cooled to room temperature to provide a polyurethane dispersion having 59.81% of solids and a measured acid number of 83.2 mg KOH/gram polymer.

To a dry, alkali- and acid-free, 2 liter kettle, equipped with an addition funnel, a condenser, a stirrer and a nitrogen gas line was added the above prepared polyurethane solid (501.5 g) and phenyl glycidyl ether (22.88 g). The mixture was heated, and, maintained at 85° C. with stirring while the acid number was followed until it reached 55.15 mg KOH/g resin. To the mixture was added a solution of KOH (11.8 g) in de-ionized water (766.6 g) over a period of 10 minutes while stirring was maintained. The reaction temperature dropped to 51.8° C. at the end of this water inversion step. The polyurethane dispersant thus prepared had 22.82% of solids.

Preparation of Pigmented Dispersions

Pigmented dispersions were prepared with magenta and cyan pigments. For the examples in Table 2, PR122 (magenta) and TRB-2 (cyan) were employed.

The following procedure was used to prepare pigmented dispersions with the polyurethane dispersants listed in Table 1. Using an Eiger Minimill, a premix was prepared at typically 20-30% pigment loading and the targeted dispersant level was selected at a pigment/dispersant (P/D) ratio of 1.5-3.0. A P/D of 2.5 corresponds to a 40% dispersant level on pigment. Optionally, a co-solvent was added at 10% of the total dispersion formulation to facilitate pigment wetting and dissolution of dispersant in the premix stage and ease of grinding during milling stage. Although other similar co-solvents are suitable, triethylene glycol monobutyl ether (TEB as supplied from Dow Chemical) was the co-solvent of choice. The polyurethane dispersants of the present invention were pre-neutralized with either KOH or amine to facilitate solubility and dissolution into water. During the premix stage, the pigment level was maintained at typically 27%, and was subsequently reduced to about 24% during the milling stage by the addition of de-ionized water for optimal media mill grinding conditions. After completion of the milling stage, which was typically 4 hours, the remaining letdown of de-ionized water was added and thoroughly mixed.

All the pigmented dispersions processed with co-solvent were purified using an ultrafiltration process to remove co-solvent(s) and filter out other impurities that may be present. After completion, the pigment levels in the dispersions were reduced to about 10 to 15%. A total of 4 different magenta (M1-M4) and 1 cyan (C1) dispersions listed in Table 2 were prepared using the polyurethane dispersants of the present invention.

19

TABLE 2

Pigmented	Pigment/	Polyurethane	Particle Size		
Dispersion	Pigment	Dispersant	Dispersant No.	D50 (nm)	D95 (nm)
M1	PR122	3	1	99	210
M2	PR122	3	2	115	209
M3	PR122	3	3	101	172
M4	PR122	3	4	96	198
C1	TRB-2	3	1	90	203

Preparation of Cross-Linked Pigment Dispersion

In the cross-linking step, a cross-linking compound was mixed with one of the pigmented dispersions listed in Table 2, and heated between 60° C.; and 80° C. with efficient stirring for between 6 to 8 hours. After the cross-linking reaction was completed, the pH was adjusted to at least about 8.0 if needed. A total of six cross-linked pigment dispersions as listed, in Table 3 were prepared. The corresponding pigmented dispersions, cross-linkable moieties and cross-linking compounds are also listed in Table 3.

TABLE 3

Cross-linked Dispersion	Pigmented Dispersion	Cross-linkable Moiety	Cross-linking Compound
XL-M1	M1	COOH, OH	Denacol ® 321
XL-M2	M2	COOH, OH	Denacol ® 321
XL-M3-A	M3	COOH, OH	Denacol ® 321
XL-M3-B	M3	COOH, OH	Denacol ® 313
XL-M4	M4	COOH, OH	Denacol ® 321
XL-C1	C1	COOH, OH	Denacol ® 321

Preparation of and Testing of Stability

The inks were prepared by conventional processes known to one skilled in the art using pigmented dispersions as well as cross-linked pigment dispersions made using the polyurethane dispersants described. The inks are processed by routine operations suitable for ink-jet ink formulation.

All ingredients except the pigmented dispersion or cross-linked pigment dispersion are first mixed together. After these ingredients have been mixed, the pigmented dispersion, or cross-linked pigment dispersion, is added. Inks were prepared by stirring together a pigmented dispersion or a cross-linked pigment dispersion together with the vehicle ingredients listed in Table 4. Each dispersion was added in an amount that resulted in 3% of pigment solids in the final ink.

TABLE 4

Vehicle Ingredient	Weight % in Ink
Butyl Cellosolve	10.0%
Butyl Carbitol	16.0%
2-Pyrrolidone	5.0%
De-ionized Water	Balance to 100%

As listed in Table 5, Inks 1-5 were made using Dispersions M1-M4 and C1, and Inks 1A, 2A, 3A-B, 4A and 5A were made using the corresponding cross-linked dispersions XL-M1, XL-M2, XL-M3-A, XL-M3-B, XL-M4 and XL-C1. The particle size (D50 and D95) of each ink at room temperature was measured. Growth of particle size after a dispersion is formulated into an ink is an indication of dispersion instability in the formulated ink vehicle. The particle sizes for pigment dispersions before and after the cross-linking step were measured and summarized in Table 5.

20

TABLE 5

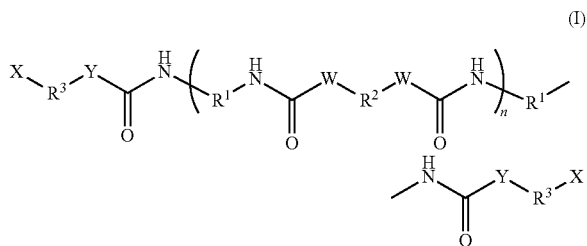
		Particle Size		
		D50 (nm)	D95 (nm)	
5	Ink			
	1	M1	371	1736
	1A	XL-M1	91	210
	2	M2	278	1144
	2A	XL-M2	111	213
	3	M3	230	735
10	3A	XL-M3-A	100	200
	3B	XL-M3-B	108	190
	4	M4	196	382
	4A	XL-M4	103	188
	5	C1	150	361
	5A	XL-C1	80	188

As shown in Table 5, inks made with the inventive cross-linked dispersions XL-M1, XL-M2, XL-M3-A, XL-M3-B, XL-M4 and XL-C1 did not show any particle size growth after they were formulated into ink vehicles. Inks made with the pigmented dispersions M1, M2, M3, M4 and C1 without any cross-linking showed large growth in particle size after they were formulated into ink vehicles. Thus, the inventive cross-linked dispersions demonstrated improved ink stability compared to their non-cross-linked counterparts.

What is claimed is:

1. An ink-jet ink comprising an aqueous ink vehicle and an aqueous pigment dispersion, wherein said aqueous dispersion comprises a colorant dispersed by a polymer dispersant, wherein said polymer dispersant is subsequently cross-linked with a cross-linking agent selected from the group consisting of epoxide, carbodiimide, N-methylol, oxazoline, silane, and mixtures thereof;

wherein the polymer dispersant prior to becoming cross-linked comprises at least one compound of the general structure of Formula I:



wherein each X is independently OH, SH, COOH or NHR⁴;

each Y is independently O, S or NR⁴;

each W is NH, O or S;

each R¹ is independently C₁-C₂₀ alkyl, C₃-C₂₀ substituted alkyl, C₆-C₄₀ aryl or C₉-C₄₀ substituted aryl;

each unit of —W—R²—W— is derived from difunctional isocyanate reactants Z¹, Z² and Z³, wherein there are at least one unit derived from Z¹, at least one unit derived from Z² and at least one unit derived from Z³;

each R³ is independently C₁-C₂₀ alkyl or C₃-C₂₀ substituted alkyl;

each R⁴ is independently —R³-A, H, C₁-C₂₀ alkyl or C₃-C₂₀ substituted alkyl;

each A is OH, SH or COOH;

n is an integer from 2 to 30;

Z¹ is a difunctional isocyanate reactant substituted with an aqueous dispersing moiety;

21

Z^2 is a difunctional isocyanate reactant substituted with one or more cross-linkable moieties;
 Z^3 is a polyol with MW less than 3000; and
 wherein cross-linking takes place between the cross-linking agent and the cross-linkable moieties in substituent R^2 pendent to the polymer backbone and the cross-linkable moieties in X terminal to the polymer chain.

2. The ink of claim 1, wherein Z^1 is a polyol substituted with the aqueous dispersing moiety.

3. The ink of claim 2, wherein Z^2 is a polyol substituted with one or more cross-linkable moieties.

4. The ink of claim 2, wherein the aqueous dispersing moiety consists of one or more carboxyl groups.

5. The ink of claim 3, wherein the cross-linkable moiety consists of one or more carboxyl groups.

6. The ink of claim 5, wherein Y is NR^4 .

7. The ink of claim 1, wherein X is OH.

8. The ink of claim 7, wherein Z^1 is a polyol substituted with the aqueous dispersing moiety.

9. The ink of claim 8, wherein Z^2 is a polyol substituted with one or more cross-linkable moieties.

22

10. The ink of claim 1, wherein X is NHR^4 .

11. The ink of claim 10, wherein Z^1 is a polyol substituted with the aqueous dispersing moiety.

12. The ink of claim 11, wherein Z^2 is a polyol substituted with one or more cross-linkable moieties.

13. The ink of claim 1, wherein Y is NR^4 .

14. The ink of claim 13, wherein R^4 is $-R^3-A$.

15. The ink of claim 14, wherein each W is O.

16. The ink of claim 14, wherein each W is NH.

17. The ink of claim 1, wherein the mole ratio of the cross-linkable moiety to the cross-linking agent is from 15:1 to 1:1.5.

18. The ink of claim 17, wherein the mole ratio of the cross-linkable moiety to the cross-linking agent is from 9:1 to 1:1.1.

19. The ink of claim 18, wherein the mole ratio of the cross-linkable moiety to the cross-linking agent is from 8:1 to 1:1.

* * * * *